Four-Electron-Donor κ^2N,C Nitrile Complexes of Tungsten

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Reflux of LWX(CO)$_x$ (L = hydrotris(3,5-dimethylpyrazol-1-yl)borate; X = I, Br, Cl; x = 2, 3) and L^{Pr}WI(CO)$_3$ (L^{Pr} = hydrotris(3-isopropylpyrazol-1-yl)borate) in organonitrile solvents produces LWX(RCN-N,C)(CO) (R = Me, Et, Ph for X = I; R = Me for X = Br, Cl) and L^{Pr}WI(MeCN-N,C)(CO), respectively. Reaction of LWI(MeCN)(CO) with NH$_4$[S$_2$PR$_2$] in hot acetonitrile results in the formation of dithio ligand derivatives, LW(S$_2$PR$_2$-S)(MeCN-N,C)-(CO) (R = OEt, OPr^i, (−)-mentholate (R*), Ph). Microanalytical, mass spectrometric, and infrared, NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}), and electronic spectroscopic data for the complexes are reported, along with the X-ray crystal structure of (R)-LW(S$_2$PR*$_2$)(MeCN)(CO). The seven-coordinate complex contains a facially tridentate L ligand, carbonyl and monodentate dithiophosphate ligands, and a side-on-bonded acetonitrile-κ^2N,C ligand. For the nitrile ligand, the W−N1 and W−C2 bond distances are 2.033(6) and 2.051(7) Å, respectively, the N1−C2 bond distance of 1.225(9) Å is considerably longer than that for free acetonitrile (1.159(2) Å (gas phase)), and the ligand is bent with an N1−C2−C3 angle of 138.1(8)°. The non-hydrogen atoms of the W(MeCN)(CO) fragment are planar, and the nitrile methyl group is *syn* with respect to the metal carbonyl fragment; these features may be rationalized in terms of π-orbital overlap. The structural and spectroscopic properties of the complexes are consistent with a four-electron-donor function for the nitrile ligands.

Introduction

In the vast majority of transition-metal nitrile complexes, an end-on κN coordination mode is observed and the nitrile ligand acts as a two-electron σ-donor coordinating through the lone pair of electrons on the nitrogen atom.[1−3] Complexes of this type are activated toward a variety of nitrile coupling, insertion, and redox reactions and find applications as synthons due to the leaving ability of the nitrile ligands.[1−3] In contrast, side-on-bonded κ^2N,C nitrile complexes are rare and their chemistry is poorly developed.[4] A number of κ^2N,C nitrile complexes were reported between 1957 and the mid-1980s;[5] by necessity, many were formulated solely on the basis of microanalytical and infrared spectroscopic data. Amid claim[5] and counterclaim,[1−3,6] several complexes emerged as likely candidates for κ^2N,C coordination; the eventual crystal structure of one of these, Cp$_2$Mo(MeCN), confirmed the existence of this type of nitrile coordination.[7,8] Soon afterward, three

more crystal structures were reported for complexes containing κ^2N,C nitrile ligands; these were CpIr(p-ClC$_6$H$_4$CN)(PPh$_3$) and Cp*Ir(p-ClC$_6$H$_4$CN)(CO), reported by Chetcuti et al.,[9] and [MoCl(MeCN)(dmpe)$_2$]BPh$_4$, reported by Anderson et al.[10] Interestingly, an isomer of [MoCl(MeCN-N,C)(dmpe)$_2$]$^+$, proposed to contain a monodentate κN nitrile, was also reported,[10] the κ^2N,C and κN complexes being distinguished by ^{1}H NMR signals at δ 3.20 and 2.10 and ^{95}Mo NMR signals at δ

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(7) Abbreviations used: bpy = 2,2′-bipyridine; Cp = η^5-cyclopentadienyl anion; Cp* = η^5-pentamethylcyclopentadienyl anion; dmpe = bis(dimethylphosphino)ethane; L = hydrotris(3,5-dimethylpyrazol-1-yl)borate; L^{Br} = hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borate; L^{Pr} = hydrotris(3-isopropylpyrazol-1-yl)borate.

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−25 and 965, respectively. These observations are consistent with greater electron donation from the nitrile ligand to the metal in the κ^2N,C complex. Later, in 1991, Green et al.[11] described the synthesis and characterization of Cp$_2$Nb(MeCN-*N,C*)(SiMe$_3$) and drew attention to the potential of ^{13}C NMR in the detection of κ^2N,C nitrile ligands. This technique was subsequently developed as a useful probe for electronic structure as well as coordination mode. In all of the above complexes, the nitrile ligands act as formal two-electron donors, reflected in nitrile carbon ^{13}C NMR signals in the range δ 165−180. Also in 1991, Harman and co-workers described the synthesis and structural characterization of [WCl(MeCN-*N,C*)(bpy)(PMe$_3$)$_2$]PF$_6$[12] and later reported the closely related complexes WCl$_2$-(MeCN-*N,C*)(PMe$_3$)$_3$ and [WCl(RCN-*N,C*)(bpy)(PMe$_3$)$_2$]-PF$_6$ (R = Bu^t, Ph).[13] These complexes exhibit very deshielded nitrile carbon resonances in the range δ 230−240, consistent with the presence of formal four-electron-donor nitrile ligands. Further examples of four-electron-donor nitrile complexes have been reported by Richmond and co-workers,[14] and Etienne's group has recently described the synthesis and structural characterization of LNb(RCN-*N,C*)(PhC$_2$Me)(CO) (L = hydro-tris(3,5-dimethylpyrazol-1-yl)borate; R = Me, Et, Ph), formulated as three-electron-donor κ^2N,C nitrile complexes on the basis of ^{13}C NMR data (R*C*N δ 175−185).[15] Indeed, the spectroscopy and bonding in κ^2N,C nitrile complexes closely parallels that of isoelectronic alkynes.[16]

Here, we describe the synthesis and characterization of a range of κ^2N,C nitrile complexes of the general type LWX(RCN)(CO) (X = halide or dithio ligand, R = Me, Et, Ph), as well as the pyrazolylborate derivative L^{Pr}WI(MeCN)(CO) (L^{Pr} = hydrotris(3-isopropylpyrazol-1-yl)borate). The complexes exhibit nitrile ^{1}H (δ (MeCN-*N,C*) ca. 3.9) and ^{13}C (δ ca. 205, $^1J_{WC}$ 25 Hz) NMR signals consistent with their formulation as formal four-electron-donor κ^2N,C nitrile complexes. We also report the crystal structure of (*R*)-LW(S$_2$PR*$_2$-*S*)(MeCN)(CO) (R* = (−)-mentholate), which confirms the side-on coordination of the acetonitrile ligands in these complexes. Finally, we briefly address aspects of the bonding and reactivity of these complexes. Templeton and co-workers[17−21] have described the generation and synthetic elaboration of nitrile−tungsten complexes of L, but to date only the synthesis and reactivity of κN complexes have been investigated. The complexes described herein are the first four-electron-donor κ^2N,C nitrile complexes to be identified in this or closely related systems, and future studies of their reactivity promise to augment and extend the impressive chemistry developed for the κN systems. Part of this work has been communicated previously.[22,23]

Results and Discussion

Syntheses. The complexes LWX(MeCN)(CO) (X = I, Br, Cl) are conveniently prepared by refluxing solutions of the halotricarbonyl−W(II) complexes, LWX(CO)$_3$,[24−26] in neat acetonitrile. Solution infrared spectroscopy reveals that the paramagnetic, halodicarbonyl−W(II) complexes, LWX(CO)$_2$,[26−28] are the immediate precursors of the nitrile complexes (eq 1). The

$$LWX(CO)_3 \xrightarrow[-CO]{\Delta} LWX(CO)_2 \xrightarrow[-CO]{\Delta,\ RCN} LWX(RCN)(CO)$$

(1)
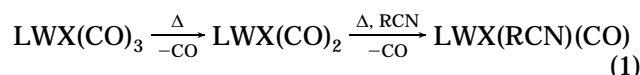
complexes can be synthesized directly from LWX(CO)$_2$, but additional synthetic effort is required. The deuterated complex LWI(MeCN-d_3)(CO) is prepared by heating LWI(CO)$_3$ or LWI(MeCN)(CO) in refluxing deuterated acetonitrile. Dithio ligand derivatives, LW(S$_2$PR$_2$-*S*)-(MeCN)(CO) (R = OEt, OPr^i, R* = (−)-mentholate, Ph), are formed when LWI(MeCN)(CO) reacts with NH$_4$[S$_2$PR$_2$] in refluxing acetonitrile. In general, the acetonitrile complexes are stable for weeks in the solid state but decompose over a period of days in aerobic solution. The reactions of LWI(CO)$_3$ with hot propionitrile and benzonitrile result in the formation of related κ^2N,C nitrile complexes, LWI(RCN)(CO) (R = Et, Ph), as indicated by solution infrared spectroscopy of the reaction mixtures. Although these complexes can be isolated and fully characterized, they appear less stable than their acetonitrile counterpart, especially in aerobic solutions. Attempts to prepare dialkyldithiophosphate derivatives by methathesis of LWI(EtCN)(CO) and LWI-(PhCN)(CO) with NH$_4$[S$_2$PR$_2$] were unsuccessful. Other tricarbonyl−W(II) pyrazolylborate complexes react in a similar fashion permitting, for example, the synthesis of L^{Pr}WI(MeCN)(CO) and L^{Br}WBr(MeCN)(CO)[26] (L^{Br} = hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borate). All the complexes are soluble in chlorinated solvents, tetrahydrofuran, acetonitrile, and aromatic hydrocarbons. They are insoluble in aliphatic hydrocarbons and alcohols and are decomposed by the latter. The reactions represented by eq 1 can be driven in the reverse direction in the presence of carbon monoxide, but the first of the reverse steps, the replacement of the nitrile ligand, requires the use of elevated temperatures, e.g., 50 °C in acetonitrile.

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Table 1. Infrared and ^{1}H NMR Spectral Data

compound	infrared (cm^{-1})[a]		^{1}H NMR, δ (mult, no. of H each resonance, J in Hz) (CDCl$_3$)			
	ν(CO)	ν(RC≡N)	L/L^{Pr} (methyl)[b]	L/L^{Pr} (methine)[c]	R (RCN)	other
LWI(MeCN)(CO)	1907 s	1688 w	1.74, 2.34, 2.44, 2.55, 2.66, 2.69	5.74, 5.83, 6.10	3.89[d]	
L^{Pr}WI(MeCN)(CO)	1918 s	1690 w	0.77, 1.10, 1.18, 1.25, 1.32, 1.41 (d, 3H, ^3J 6.6)	5.95, 6.06, 6.39, 7.61, 7.62, 7.72, (d, 1H, ^3J 2.5)	3.90	CHMe$_2$ 2.19, 3.19, 4.23 (sept, 1H, ^3J 6.6)
LWBr(MeCN)(CO)	1905 s	1688 w	1.81, 2.39, 2.48, 2.56, 2.60, 2.73	5.80, 5.90, 6.10	3.94	
LWCl(MeCN)(CO)	1905 s	1687 w	1.79, 2.35, 2.42, 2.47, 2.48, 2.68	5.77, 5.85, 6.03	3.90	
LWI(EtCN)(CO)	1905 s	1685 w	1.75, 2.34, 2.43, 2.55, 2.66, 2.68	5.72, 5.82, 6.09	CH_3 1.76 (t, 3H); CH_2 3.82, 4.26 (sept, 1H)	
LWI(PhCN)(CO)	1921 s	1656 w	1.68, 2.38, 2.48, 2.60, 2.69, 2.78	5.75, 5.87, 6.15	Ph 7.69 (m, 3H), 8.36 (d, 2H)	
LW(S$_2$PR$_2$)(MeCN)(CO)						
R = OEt	1914 s	1693 w	1.81, 2.34, 2.36, 2.50, 2.55, 2.71	5.71, 5.83, 6.04	3.93	CH_3 1.33 (td, 6H, ^3J 7.0, J_{PH} 4.3); CH_2 4.11 (m, 4H)
R = OPr^i	1912 s	1699 w	1.80, 2.33, 2.35, 2.49, 2.54, 2.72	5.69, 5.81, 6.03	3.94	CH_3 1.27, 1.30, 1.34, 1.36 (d, 3H, ^3J 6.3); CH 4.78, 4.83 (dsept, 1H, J_{PH} 13, ^3J 6.3)
R = mentholate (major)	1912 s	1702 w	1.79, 2.34, 2.36, 2.50, 2.56, 2.72	5.69, 5.82, 6.01	3.92	CH_3 0.8−1.0 (m, 18H); CH$_x$ 1.2−3.0 (m, 14H); OCH 4.34, 4.36 (pent, 1H)
R = mentholate (minor)	1912 s	1702 w	1.81, 2.33, 2.40, 2.50, 2.52, 2.56	5.67, 5.80, 6.03	3.96	CH_3 0.8−1.0 (m, 18H); CH$_x$ 1.2−3.0 (m, 14H); OCH 4.34, 4.36 (pent, 1H)
R = Ph	1915 s	1703 w	1.76, 2.33, 2.35, 2.51, 2.54, 2.62	5.68, 5.76, 6.07	3.58	Ph 7.32 (m, 6H), 7.68 (m, 2H), 7.94 (m, 2H)

[a] In CH$_2$Cl$_2$ solution. Listings of peaks from KBr spectra are given in the Experimental Section. [b] All singlet resonances integrating for three protons unless indicated. [c] All singlet resonances integrating for one proton unless specified. [d] This resonance was absent from the spectrum of the CH$_3$CN-d_3 analogue.

Table 2. ^{13}C and ^{31}P NMR and Electronic Spectral Data[a]

	^{13}C{^{1}H} NMR in CDCl$_3$, δ ($^1J_{WC}$, Hz)[b]				
	R (RCN)	RCN	WCO	^{31}P{^{1}H} NMR, δ (CDCl$_3$)	electronic spectrum,[c] nm (ϵ M^{-1} cm^{-1})
LWI(MeCN)(CO)	22.56[d]	206.36 (25)	226.33 (154)		780 (60), 395 (330 sh), 320 (5000 sh)
L^{Pr}WI(MeCN)(CO)	22.58[e]	207.22 (27)	225.10 (154)		775 (50), 380 (1800 sh), 335 (3700)
LWBr(MeCN)(CO)	21.24	205.86 (26)	225.76 (158)		770 (60), 380 (500 sh)
LWCl(MeCN)(CO)	21.76	206.99 (25)	227.55 (159)		740 (80), 410 (120 sh)
LWI(EtCN)(CO)[f]	12.44[g] 29.80	208.66 (26)	224.91 (154)		
LWI(PhCN)(CO)[f]	128.62, 131.43 132.28, 133.00	208.55	228.28		
LW(S$_2$PR$_2$)(MeCN)(CO)					
R = OEt	22.50	203.07 (26)	224.78 (153)	113.5	685 (55), 440 (230 sh), 325 (5250 sh)
R = OPr^i	22.64	202.71 (26)	225.14 (160)	111.5	680 (50), 440 (235 sh), 325 (5500 sh)
R = mentholate (maj)[h]		202.12 (26)	225.72 (155)	110.6 (118.8[i])	685 (50), 440 (285 sh), 330 (5400 sh)
R = Ph	22.45	202.77 (26)	224.67 (152)	84.7	685 (50), 440 (210 sh), 305 (9750 sh)

[a] A full listing of ^{13}C data is provided as Supporting Information. [b] All resonances are singlets unless indicated. [c] Spectra were recorded in dichloromethane solution, sh = shoulder (estimates only). [d] This resonance was observed as a septet (J_{CD} 23 Hz) in the deuterated analogue LWI(MeCN-d_3)(CO). [e] This resonance was assigned by analogy to LWI(MeCN)(CO)—assignment not confirmed by deuteration. [f] Sensitivity at low concentrations prevented the collection of reliable electronic spectral data. [g] The methyl resonance of EtCN was assigned using heteronuclear multiple-bond coupling NMR experiments. [h] Unambiguous assignment of the methyl carbon resonance is not possible without selective deuteration. [i] Chemical shift of the minor diastereomer.

Physical and Spectroscopic Characterization. Accurate microanalyses were obtained for all the complexes except for the propionitrile and benzonitrile derivatives, which retain variable amounts of hexane as a solvent of crystallization. Mass spectra of LWX-(MeCN)(CO) (X = Cl, I) reveal parent ion clusters with the expected isotope patterns at m/z 585 and 677, respectively. The mononuclear formulation implicit in these data was confirmed by the X-ray crystal structures of L^{Br}WBr(MeCN)(CO)[26] and LW(S$_2$PR*$_2$)(MeCN)(CO) (vide infra).

Spectroscopic data are summarized in Tables 1 and 2. The solution infrared spectra of the complexes are characterized by a single, strong ν(CO) band at ca. 1905 cm^{-1} (Table 1). Solid-state (KBr) spectra also exhibit a single ν(CO) band, bands due to L and the dithio ligands, and a sharp but weak band at ca. 1700 cm^{-1}, which is assigned to the ν(CN) mode of the $\kappa^2 N,C$ ligand. The lower-frequency ν(CN) modes of the complexes compared to free organonitrile or κN nitrile complexes can be attributed to a reduction in the bond order of the nitrile group upon binding to tungsten. The ν(CN) band lies close to the range typical of C=N double bonds, viz., 1470−1690 cm^{-1}.[29] The presence of a single ν(CN) band at 1508 cm^{-1} in the spectrum of L^{Pr}WI(MeCN)-

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(CO) indicates the presence of the L^{Pr} ligand rather than, e.g., hydrobis(3-isopropylpyrazolyl)(5-isopropylpyrazolyl)borate, which may result from borotropic shifts in such systems.[30,31]

^1H and ^{13}C NMR spectra are indicative of molecular C_1 symmetry in solution (Tables 1 and 2). Accordingly, for the LWX(MeCN)(CO) complexes, seven singlet methyl resonances and three singlet methine resonances are observed in the ^1H NMR spectra. The absence of the δ 3.9 peak in the NMR spectrum of LWI(MeCN-d_3)(CO) confirms its assignment as the acetonitrile methyl resonance. The other acetonitrile complexes display a similar resonance in the range δ 3.58–3.90, assigned by analogy with LWI(MeCN)(CO) to the acetonitrile methyl group. In all cases, the chemical shift of the acetonitrile methyl group is in the range observed for other four-electron-donor acetonitrile complexes, e.g., *trans*-[WCl(MeCN)(bpy)(PMe$_3$)$_2$]PF$_6$ (δ 4.14)[12,13] and *cis*-WCl$_2$(MeCN)(PMe$_3$)$_3$ (δ 3.23).[13] Indeed, attainment of a formal 18-electron count by the title complexes requires the nitrile ligands to act as four-electron donors. In the spectrum of $L^{Pr}WI(MeCN)(CO)$, the pairs of diastereotopic methyl groups produce six doublet resonances; three isopropyl methine resonances, appropriate ring methine resonances, and an acetonitrile methyl resonance at δ 3.9 are also observed. The NMR spectra of the dithio ligand derivatives LW(S$_2$PR$_2$)-(MeCN)(CO) exhibit L and MeCN resonances in accord with those described above, as well as the resonances expected for the S$_2$PR$_2^-$ ligands in complexes of C_1 symmetry. The diastereotopicity of the CH$_2$ and CMe$_2$ groups in the R = OEt and OPr^i derivatives is clearly evident. The presence of two diastereomers in samples of LW(S$_2$PR*$_2$)(MeCN)(CO) is indicated by the ^1H and ^{31}P NMR spectra. The ratio of the two diastereomers is estimated by spectral integration to be 8:1. The crystal structure of the (*R*) isomer has been determined (vide infra). There is no indication of the presence of isomeric forms of the other complexes, and it is proposed that a *syn* structure, as displayed by (*R*)-LW(S$_2$PR*$_2$)(MeCN)-(CO), is present in each case. Related η^2-alkyne complexes LWI(η^2-RC$_2$R′)(CO) (R = Ph, CH$_2$C(Me); R′ = H) exist as mixtures of two isomers, distinguished by the orientation of the alkyne ligand; the isomers with the bulkier R groups *syn* with respect to the WCO fragment predominate, i.e., they are thermodynamically more stable.[24] There is no evidence for rotation of the acetonitrile ligands of LWX(MeCN)(CO) at room temperature, which is a feature of other $\kappa^2 N,C$ complexes.[12–15] The LWI(RCN)(CO) (R = Et, Ph) complexes exhibit broadly similar NMR features. For LWI(EtCN)(CO), a triplet resonance at δ 1.76 and two septet resonances at δ 3.82 and 4.26 are assigned to the methyl and diastereotopic methylene protons of the propionitrile ligand. These resonances are considerably deshielded with respect to resonances of free propionitrile (δ 1.26 and 2.33), κN complexes (δ 1.26 and 2.35), and a recently reported three-electron-donor nitrile complex (δ 1.38, 2.31, and 3.31).[15] Complex multiplets at δ 7.69 and 8.36, integrating for three and two protons,

respectively, are observed in the ^1H NMR spectrum of LWI(PhCN)(CO).

The $^{13}C\{^1H\}$ NMR spectrum of LWI(MeCN)(CO) exhibits resonances at δ 22.56 and 206.36 ($^1J_{WC}$ 25 Hz), which can be assigned to the acetonitrile methyl and nitrile carbon atoms, respectively. In the spectrum of the MeCN-d_3 analogue, the δ 22.56 signal appears as a septet due to deuterium coupling ($^1J_{DC}$ 23 Hz), permitting an unambiguous assignment of this resonance. The methyl and nitrile carbon resonances of free acetonitrile are observed[32] at δ 1.85 and 116.67, respectively, and range between δ 4.0–6.0 and δ 115–130 in κN acetonitrile complexes.[33] Nitrile carbon resonances are observed in the δ 165.1–180.9 range for previously reported two- and three-electron-donor complexes, while resonances between δ 235 and 243 are typical of known four-electron-donor complexes. These comparisons support a four-electron-donor description for the nitrile ligands in the title complexes. For LWI(EtCN)(CO), resonances at δ 12.44 and 29.80 are assigned to the propionitrile methyl and methylene carbons, respectively; these resonances are observed at δ 10.50 and 10.91 in free propionitrile[32] and at δ 14.1 and 26.6 in LNb(EtCN)(η^2-PhC$_2$Me)(CO).[15] For LWI(PhCN)(CO), singlets at δ 128.62, 131.43, 132.28, and 133.00 are assigned to benzonitrile ring carbons and indicate that rotation around the C$_{nitrile}$–C$_{phenyl}$ bond is rapid on the NMR time scale. Definite assignment of each carbon is not possible, however, there is a clear high-frequency shift of the *ipso* carbon resonance in comparison to the free ligand, demonstrating the deshielding influence of the four-electron-donor PhCN ligand. All the spectra exhibit resonances at ca. δ 225 ($^1J_{WC}$ ca. 155 Hz) for the carbonyl carbon atoms. The respective assignments of the carbonyl and nitrile carbon resonances are based on the disparate ^{183}W–^{13}C coupling constants, expected to be around 150–170 Hz for a carbonyl resonance, and by analogy with NMR data for related LWI(CO)(η^2-MeC≡CMe).[24]

Single peaks are observed in the $^{31}P\{^1H\}$ NMR spectra of the various S$_2$PR$_2^-$ complexes, except in the case of LW(S$_2$PR*$_2$)(MeCN)(CO) where a peak from each of the two diastereomers is observed. The dithiophosphate ligands (δ 110.6–118.8) exhibit deshielded resonances relative to the S$_2$PPh$_2^-$ complex (δ 84.7), consistent with the greater electron-withdrawing capacity of the alkoxy groups.

In the electronic spectrum of gold LWI(MeCN)(CO), three maxima are observed at 780, 395, and 320 nm. Similarly, the spectrum of gold $L^{Pr}WI(MeCN)(CO)$ exhibits three maxima at 775, 380, and 335 nm. Green LWX(MeCN)(CO) (X = Cl, Br) exhibit electronic spectra with bands at 770–740 and 410–380 nm. Three bands at 685, 440–405, and 330–305 nm are also observed for the green LW(S$_2$PR$_2$)(MeCN)(CO) complexes. The extinction coefficients for the lowest energy bands are consistent with their assignment as d–d transitions. The electronic spectra of related tungsten η^2-alkyne

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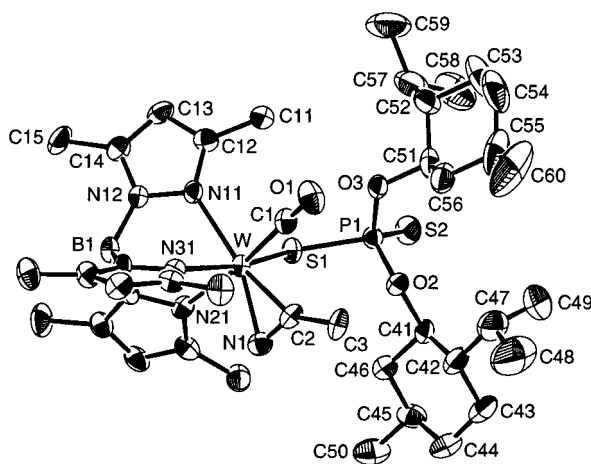
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Figure 1. Molecular structure and atom-numbering scheme for (R)-LW(S₂PR*₂)(MeCN)(CO). The numbering of the pyrazole rings containing N21 and N31 follows that shown for the ring containing N11. Hydrogen atoms have been excluded for clarity.[13]

Table 3. Selected Bond Distances (Å) and Angles (deg) for (R)-LW(S₂PR*₂)(MeCN)(CO)

W–S1	2.435(2)	W–N31	2.183(6)
W–C1	1.940(8)	C2–N1	1.225(9)
W–C2	2.051(7)	C1–O1	1.156(9)
W–N1	2.033(6)	P1–S1	2.049(3)
W–N11	2.241(6)	P1–S2	1.937(3)
W–N21	2.262(6)		
S1–W–C1	95.9(3)	C2–W–N31	95.5(3)
S1–W–C2	101.2(3)	N1–W–N11	161.2(3)
S1–W–N1	100.2(2)	N1–W–N21	80.2(2)
S1–W–N11	87.0(2)	N1–W–N31	90.8(3)
S1–W–N21	82.9(2)	N11–W–N21	83.6(2)
S1–W–N31	162.6(1)	N11–W–N31	78.7(3)
C1–W–C2	72.5(3)	N21–W–N31	85.6(3)
C1–W–N1	107.3(3)	W–N1–C2	73.4(5)
C1–W–N11	88.9(3)	W–C2–N1	71.7(5)
C1–W–N21	172.4(3)	N1–C2–C3	138.1(8)
C1–W–N31	93.8(4)	C3–C2–W	150.0(7)
C2–W–N1	34.9(3)	W–C1–O1	174(1)
C2–W–N11	160.3(3)	W–S1–P1	116.5(1)
C2–W–N21	115.0(3)	S1–P1–S2	111.3(1)

carbonyl complexes reveal low intensity d–d bands in the 540–630 nm region.[24] The η^2-alkyne complex, WCl₂(η^2-MeC₂Et)(PMe₃)₃ displays a single weak absorption at 564 nm ($\epsilon = 86$ M⁻¹ cm⁻¹), while the spectrum of the acetonitrile analogue exhibits a band at 654 nm ($\epsilon = 86$ M⁻¹ cm⁻¹); these observations were rationalized in terms of a smaller HOMO-LUMO energy gap in the more electron-deficient acetonitrile complex.[13]

Crystal Structure of (R)-LW(S₂PR*₂)(MeCN)- (CO). The crystallographic characterization of mononuclear tris(pyrazolyl)borate complexes of the type LWXYZ is sometimes complicated by disorder of the coligands, X, Y, and Z, around a pseudo 3-fold axis; this can be particularly problematic when the coligands are similar in size and nature. Thus, the crystal structure of LᴮʳWBr(MeCN)(CO)[26] is afflicted by disorder of the nitrile and carbonyl ligands such as to reduce its value in accurately defining the $\kappa^2 N,C$ fragment. Recognizing the inherent chirality of the LWX(MeCN)(CO) system, we reasoned that the incorporation of a chiral coligand would produce diastereomers that may circumvent these problems and allow an accurate X-ray structure determination. These expectations were realized with the synthesis and characterization of (R)-LW(S₂PR*₂)- (MeCN)(CO),[34] the structure of which is shown in Figure 1. Selected bond distances and angles are presented in Table 3. The structure consists of a seven-coordinate tungsten center with a facially tridentate L ligand, carbonyl and monodentate S₂PR*₂⁻ ligands, and a side-on $\kappa^2 N,C$-bound acetonitrile ligand. With the MeCN ligand regarded as monodentate, the tungsten coordination sphere may be described as having a distorted octahedral geometry. The W(MeCN) fragment is characterized by the following structural parameters: W–N1 = 2.033(6) Å, W–C2 = 2.051(7) Å, C2–N1 = 1.225(9) Å, N1–W–C2 = 34.9(3)°, W–C2–C3 = 150.0(7)°, and N1–C2–C3 = 138.1(8)°. The N1–C2 bond is lengthened by 0.066 Å compared to free acetonitrile (MeC≡N

= 1.159(2) Å, measured in the gas phase[35]), consistent with a reduction in the CN bond order as a result of π-interactions with the tungsten center. The W–C2 and W–N1 bonds are marginally longer than the corresponding distances in cis-WCl₂(MeCN)(PMe₃)₃[13] but significantly shorter than those of Cp₂Mo(MeCN),[9] highlighting the extent of CN π-orbital overlap between two- and four-electron-donor acetonitrile complexes. The non-hydrogen atoms of the W(MeCN)(CO) framework are planar to ±0.05 Å, and there is a *syn* relationship between the nitrile methyl and metal carbonyl groups. The planarity of the W(MeCN)(CO) framework is a feature common to complexes containing [M(RCN-N,C)- (CO)]ⁿ⁺ [14,15] and [M(η^2-RC₂R')(CO)]ⁿ⁺ [16] fragments and may be attributed to electronic factors (vide infra). The W–S1 bond length of 2.435(2) Å is typical of a single bond[36] and indicates minimal π-bonding between these atoms. The P1–S2 bond length of 1.937(3) Å is indicative of a P–S double bond.[37] The dithiophosphate oxygen atoms O2 and O3 are directed toward the carbonyl and nitrile ligands, and as a consequence, S2 is directed away from the metal center, i.e., the ligand adopts an *exo* conformation. A very similar arrangement is observed in the dicarbonyl complexes LW{S₂P-(OPrᶦ)₂}(CO)₂[26] and CpFe{S₂P(OPrᶦ)₂}(CO)₂.[38] A slightly bent W–C1–O1 angle (174(1)°) inclines the carbonyl group towards the acetonitrile methyl group. The W–N(n1) distances are quite disparate, the longest being *trans* to the π-donor and acceptor ligands, the shortest being *trans* to S1. This structure is the first to feature the S₂PR*₂⁻ ligand and only the third to feature a $\kappa^2 N,C$-donor nitrile ligand at tungsten.

Molecular Orbital Treatment. The bonding in known $\kappa^2 N,C$ nitrile complexes has been likened[12,13] to the bonding in η^2-alkyne complexes.[16] As described by Templeton, η^2-alkyne ligands can function as two-, three-, or four-electron donors by combining σ-, π-, and back-bonding interactions involving metal d and alkyne

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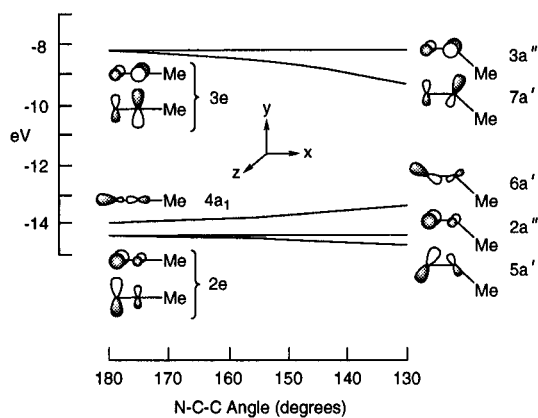
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Figure 2. Molecular orbitals for linear (left-hand side) and bent (140°) (right-hand side) acetonitrile molecules. The variation of the energies of the indicated orbitals as a function of nitrile N−C−C angle is indicated.

$\pi_{\parallel}$, $\pi^*_{\parallel}$, and $\pi_{\perp}$ orbitals ($\parallel$ and $\perp$ differentiate orbitals lying in and perpendicuar to the plane of the MC$_2$ fragment, respectively).[16,39,40] While the descriptions of the bonding in κ²N,C nitrile and η²-alkyne complexes are essentially similar, subtle differences arise from the heteroatomic nature of the nitrile group. Here, we present a qualitative description of the bonding in geometrically idealized LWI(MeCN)(CO); this description is based on the results of extended Hückel molecular orbital calculations.[41] As a prelude to the discussion of metal complexes, it is interesting to explore the bonding in linear and bent forms of MeCN. The frontier orbitals of linear (C_{3v}) MeCN are presented on the left-hand side of Figure 2; the coordinate system is also shown. A pair of degenerate C≡N π orbitals (2e) lie to low energy and a pair of degenerate C≡N π* orbitals (3e) lie to high energy. A σ orbital (4a$_1$) involving the N sp hybrid and C p$_x$ orbitals lies between these π and π* levels. In η²-alkynes, the analogous orbital is considerably lowered in energy due to the σ-interaction involving the second substituent. The effects of bending at the nitrile carbon atom are also shown in the diagram; MOs appropriate for a N−C−C angle of 140° are presented on the right-hand side of the figure, and in the following, $\parallel$ and $\perp$ specify π orbitals lying in and perpendicular to the plane of the molecule, respectively. Upon bending, the σ orbitals of the methyl group interact in a bonding fashion with both the $\pi_{\parallel}$ and $\pi_{\parallel}$* orbitals, lowering their energies. Due to a decrease in σ-bonding interactions between the methyl group and the nitrile group, the σ orbital rises in energy upon bending. Thus, the σ-donor, and π-acceptor ability of the MeCN ligand are functions of the N−C−C angle; both are enhanced with increased bending of the MeCN fragment. Apart from the energy changes summarized in Figure 2, the lower symmetry of bent MeCN (C_s) allows the in-plane σ, $\pi_{\parallel}$, and $\pi_{\parallel}$* orbitals to mix, changing the shapes of the molecular orbitals as a

function of N−C−C angle. This mixing is essentially the same as that described previously for isoelectronic HNN$^+$ by DuBois and Hoffmann.[42] There is considerable mixing of the σ and $\pi_{\parallel}$ orbitals as a consequence of their close energy matching. In the manner described for HNN$^+$, bending of MeCN at carbon results in a stronger π-acceptor orbital (7a′) in the plane of bending and a σ-donor orbital (5a′) directed *trans* to the methyl group. The $\pi_{\perp}$ and $\pi_{\perp}$* orbitals are only slightly affected by bending of the N−C−C angle.

In the model for LWI(CO)(MeCN), the carbonyl, nitrile, and iodide ligands reside on the x, $-y$, and z axes, respectively. Thus, the π-acid ligands lie in the xy plane, and the nitrile ligand retains the orientation with the coordinate system previously used in Figure 2. Thus, we can continue to use $\parallel$ and $\perp$ to define orbitals lying in and perpendicular to the xy plane, the plane containing MeCN, respectively. A number of interactions between the orbitals of bent MeCN (N−C−C = 140°) and the tungsten d orbitals are possible. A σ interaction between the 5a′ nitrile orbital and the d$_{x^2-y^2}$ metal orbital and a $\pi_{\perp}$ interaction between the 2a″ nitrile orbital and the d$_{yz}$ metal orbital lie at low energy; they can be considered to involve electron donation from the filled nitrile orbitals to the empty metal orbitals, providing a total of four electrons to the metal center (the four-electron-donor description is adopted in the spirit of Templeton's[16] use of this term for alkyne complexes). An orbital interaction involving the 6a′ orbital and a hybrid metal orbital is also observed, but the metal orbital contribution is small in this case. In this d^4 system, two formally filled d$_\pi$ orbitals are stabilized by π interactions with empty π* carbonyl and nitrile ligand orbitals. Two π back-bonding interactions of this type may be envisaged. The first involves the metal d$_{xy}$ and carbonyl $\pi_{\parallel}$* orbitals and defines the $\pi_{\parallel}$ M → CO interaction. The second involves the metal d$_{xz}$ and carbonyl $\pi_{\perp}$* orbitals and defines the $\pi_{\perp}$ M → CO interaction. The former participates in a significant interaction with the 7a′ orbital of the nitrile and stabilizes the nitrile ligand through π back-bonding. The latter interacts only weakly with the 3a″ orbital, and constitutes the HOMO in the LWI(CO)(MeCN) molecule. The LUMO is comprised principally of metal d$_{yz}$ and nitrile N p$_z$ orbitals in an antibonding combination. Competition from the nitrile for metal π electron density is consistent with a reduction in back-bonding to the carbonyl ligand and the higher than expected ν(CO) frequency in these d^4 monocarbonyl complexes. In addition, the bonding picture accounts for the deshielding of the nitrile carbon and methyl group and supports the assignment of an 18-electron configuration to the metal in these four-electron-donor nitrile complexes.

Aspects of κ²N,C Nitrile Reactivity. We now briefly relate some aspects of the reactivity of the κ²N,C nitrile complexes. In the acetonitrile complexes, nitrile exchange does not take place to any appreciable extent at room temperature but is observed upon heating (e.g., in refluxing MeCN-d$_3$). The complex LWI(MeCN)(CO) reacts with phenylacetylene in refluxing acetonitrile to produce known LWI(η²-PhC$_2$H)(CO).[24] We have also explored the potential of the nitrile complexes as precursors for high-valent oxo− and thio−tungsten

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complexes.[22,23] In efforts to synthesize the (carbonyl)-oxotungsten(IV) complex, LWOI(CO), LWI(MeCN)(CO) was reacted with a variety of oxygen atom transfer reagents, including dimethyl sulfoxide, propylene oxide, cyclohexene oxide, and pyridine *N*-oxide. The reaction with pyridine *N*-oxide yields a number of products, one of which is the acetylimido complex LW{NC(O)Me}-I(CO).[43] The blue-green, crystalline, diamagnetic complex has been derivatized via methathesis with NaSPh to yield LW{NC(O)Me}(SPh)(CO), which has been structurally characterized.[43] Only a trace of purple LWOI-(CO) was produced in the reaction. This oxygen atom transfer reaction may be extended to the propionitrile and benzonitrile derivatives. In contrast, reaction of LWX(MeCN)(CO) complexes with the sulfur atom transfer reagent propylene sulfide results in good yields of the (carbonyl)thiotungsten complexes, LWSX(CO).[22,23] Finally, we have also isolated a number of novel carbonyl−W(III) complexes, e.g., LWI$_2$(CO), formed in the reaction of LWI(MeCN)(CO) with iodine.[26] Chemistry aimed toward the modification or synthetic elaboration of the nitrile ligands will be the subject of future studies.

Conclusion

This paper reports the synthesis and characterization of new four-electron-donor $\kappa^2 N,C$ nitrile complexes of tungsten. The spectral and structural features of the complexes, only the second class of $\kappa^2 N,C$ complexes known for tungsten, are completely in accord with their formulation and the donor capacity proposed for the nitrile ligands. Apart from their intrinsic novelty, these complexes are useful synthons for a variety of new organometallic and coordination compounds and promise to broaden the scope of nitrile elaboration processes at tungsten. Generation of coordinatively and electronically unsaturated tris(pyrazolyl)borate complexes of molybdenum and tungsten in nitrile solvents may be expected to yield related $\kappa^2 N,C$ nitrile complexes, permitting the further development of this potentially broad area of group 6 chemistry.

Experimental Section

General Comments. All reactions were performed under an atmosphere of dinitrogen using dried, deoxygenated solvents and standard Schlenk techniques. Samples of LWX-(CO)$_3$ (X = Cl, Br, I),[26] L^{Pr}WI(CO)$_3$,[26] and NH$_4$[S$_2$PR$_2$] (R = OEt, OPr^i, Ph[44]) were prepared by literature methods or slight modifications thereof. All other reagents were analytical reagent grade or above. Microanalyses were performed by Atlantic Microlabs Inc, Norcross, GA.

Syntheses. **LWI(MeCN)(CO).** A solution of LWI(CO)$_3$ (2.24 g, 3.24 mmol) in acetonitrile (30 mL) was refluxed for 4 h, then cooled to room temperature and kept overnight at −4 °C. The gold-colored crystalline solid was filtered off, washed with cold acetonitrile (5 mL) and dried *in vacuo*. Isolated yield: 1.36 g, 62%. This product was suitable for synthetic work, but analytical samples required purification by column chromatography on silica using 2/1 dichloromethane/*n*-hexane

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as the eluent. The compound was recrystallized from dichloromethane by the addition of *n*-hexane.

Anal. Calcd for C$_{18.5}$H$_{26}$BClIN$_7$OW: C, 30.88; H, 3.64; N, 13.63. Found: C, 31.15; H, 3.70; N, 13.68. IR (KBr): ν(BH) 2553, ν(CO) 1896, ν(C≡N) 1687, ν(CN) 1545 cm^{-1}. MS, *m/z* for parent ion of LWI(MeCN-*d*^{8})(CO): 677 (20), 678 (88), 679 (79), 680 (100), 681 (44), 682 (84), 685 (19).

L^{Pr}WI(MeCN)(CO). A solution of L^{Pr}WI(CO)$_3$ (0.54 g, 0.74 mmol) in acetonitrile (20 mL) was refluxed for 2.5 h and cooled to room temperature. The reaction mixture was reduced to dryness, the residue chromatographed on silica gel using 3/1 dichloromethane/*n*-hexane, and the gold-colored fraction collected. The compound was isolated via recrystallization from dichloromethane/*n*-hexane as a gold-colored crystalline solid, which was filtered off, washed with *n*-hexane (5 mL), and dried *in vacuo*. Yield: 0.31 g, 58%.

Anal. Calcd for C$_{21}$H$_{31}$BIN$_7$OW: C, 35.08; H, 4.35; N, 13.64. Found: C, 35.15; H, 4.35; N, 13.60. IR (KBr): ν(BH) 2501, ν(CO) 1906, ν(C≡N) 1684, ν(CN) 1508 cm^{-1}.

LWBr(MeCN)(CO). A solution of LWBr(CO)$_3$ (0.43 g, 0.66 mmol) in acetonitrile (25 mL) was refluxed for 1 h and cooled to room temperature. The solvent was evaporated to dryness, and the residue was column chromatographed on silica gel using 1/1 dichloromethane/*n*-hexane as the eluent. The olive-green fraction (0.30 g, 72%) was collected and recrystallized from dichloromethane/*n*-hexane as an olive-green microcrystalline solid. The solid was filtered, washed with *n*-hexane and dried *in vacuo*.

Anal. Calcd for C$_{18}$H$_{25}$BBrN$_7$OW: C, 34.32; H, 4.00; N, 15.56. Found: C, 34.25; H, 3.86; N, 15.50. IR (KBr): ν(BH) 2552, ν(CO) 1905, ν(C≡N) 1690, ν(CN) 1544 cm^{-1}.

LWCl(MeCN)(CO). A solution of LWCl(CO)$_3$ (1.00 g, 1.67 mmol) in acetonitrile (20 mL) was refluxed for 1 h and cooled to room temperature. The solvent was evaporated to dryness, and the residue was chromatographed on silica gel using 2/1 dichloromethane/petroleum spirits (60−80 °C bp) as the eluent. The green fraction (0.45 g, 45%) was collected and recrystallized from dichloromethane/hexane as a green microcrystalline solid. The solid was filtered, washed with *n*-hexane (3 mL), and dried *in vacuo*.

Anal. Calcd for C$_{18}$H$_{25}$BClN$_7$OW: C, 36.92; H, 4.30; N, 16.74; Cl, 6.05. Found: C, 37.07; H, 4.37; N, 16.63; Cl, 6.15. IR (KBr): ν(BH) 2552, ν(CO) 1900, ν(C≡N) 1691, ν(CN) 1544 cm^{-1}. MS *m/z* for parent ion: 581 (19), 582 (73), 583 (67), 584 (100), 585 (52), 586 (92), 587 (25), 588 (26).

LWI(EtCN)(CO). A solution of LWI(CO)$_3$ (2.0 g, 2.88 mmol) in propionitrile (30 mL) was refluxed for 1.5 h and then allowed to cool to room temperature. The reaction mixture was reduced to dryness, and the residue was chromatographed on silica gel using 2/1 dichloromethane/*n*-hexane as the eluent. The orange-brown fraction was collected and recrystallized from dichloromethane/*n*-hexane yielding a pale brown crystalline solid, which was filtered, washed with cold *n*-hexane (2 mL), and dried *in vacuo*. Yield: 0.80 g, 40%.

IR (KBr): ν(BH) 2550, ν(CO) 1903, ν(C≡N) 1683, ν(CN) 1543 cm^{-1}.

LWI(PhCN)(CO). A solution of LWI(CO)$_3$ (1.0 g, 1.45 mmol) in benzonitrile (20 mL) was heated at 100 °C for 3 h, then reduced to dryness *in vacuo*. The residue was then chromatographed twice on silica gel using dichloromethane as the eluent (the dark brown fraction was collected). The compound was isolated via recrystallization from dichloromethane/*n*-hexane as a brown crystalline solid, which was filtered, washed with cold *n*-hexane (5 mL), and dried *in vacuo*. Yield: 0.80 g, 75%.

IR (KBr): ν(BH) 2550, ν(CO) 1910, ν(C≡N) 1657, ν(CN) 1542 cm^{-1}.

NH$_4$[S$_2$PR$_2$*] (R* = (−)-mentholate). A suspension of phosphorus pentasulfide (2.40 g, 5.40 mmol) and (−)-menthol (6.71 g, 42.9 mmol) in toluene (80 mL) was refluxed for 1.5 h. The reaction mixture was allowed to cool and any solid residue

Table 4. Crystallographic Data for
(*R*)-LW(S$_2$PR*$_2$)(MeCN)(CO)

formula	C$_{38}$H$_{63}$BN$_7$O$_3$PS$_2$W
fw	955.7
cryst size, mm	0.32 × 0.13 × 0.13
cryst syst	orthorhombic
space group	P2$_1$2$_1$2$_1$
a, Å	17.753(7)
b, Å	18.867(5)
c, Å	13.394(4)
V, Å^3	4486(2)
Z	4
D$_{calcd}$, g cm^{-3}	1.415
F(000)	1960
μ, cm^{-1}	27.48
transmission factors	0.970 − 1
no. of data colld	5741
no. of unique data with $I \geq 3.0\sigma(I)$	4040
R	0.033
R$_w$	0.031
residual electron density, e Å^{-3}	0.51

was removed by filtration. Ammonia gas was bubbled through the filtrate for 10 min, and hexane (80 mL) was added to precipitate the product. The white crystalline solid was filtered off, washed with hexane (20 mL) and dried *in vacuo*. Yield: 5.20 g, 57%.

Anal. Calcd for C$_{20}$H$_{42}$NO$_2$PS$_2$: C, 56.70; H, 9.99; N, 3.31; S, 15.14. Found: C, 56.80; H, 9.95; N, 3.26; S, 15.06. IR (KBr): 3420 br, 3105 br, 2955 s, 2926 s, 2870 m, 1453 m, 1414 s, 1387 s, 1012 m, 996 m, 965 s, 930 m, 882 m, 870 m, 818 m, 672 s, 570 m cm^{-1}.

LW(S$_2$PR$_2$-*S*)(MeCN)(CO) Complexes. In a typical synthesis, a stoichiometric mixture of LWI(MeCN)(CO) (1–3 mmol) and NH$_4$[S$_2$PR$_2$] was suspended in acetonitrile (30–50 mL), and the mixture was heated at 75 °C for 0.5 h. The dark green solution was then reduced to dryness, and the residue was chromatographed on silica using 3/1 dichloromethane/*n*-hexane as the eluent. The green fraction was collected and recrystallized from dichloromethane/*n*-hexane as green crystals.

R = OEt. Yield: ca. 60%. Anal. Calcd for C$_{22}$H$_{35}$BN$_7$O$_3$-PS$_2$W: C, 35.94; H, 4.80; N, 13.33; S, 8.72. Found: C, 35.76; H, 4.75; N, 13.14; S, 8.88. IR (KBr): ν(BH) 2559, ν(CO) 1909, ν(C≡N) 1686, ν(CN) 1545, ν(P−O$_{alkyl}$) 939, 956, ν(P=S) 658, ν(P−S) 549 cm^{-1}.

R = OPr^i. Yield: ca. 52%. Anal. Calcd for C$_{24}$H$_{39}$BN$_7$O$_3$-PS$_2$W: C, 37.76; H, 5.15; N, 12.84; S, 8.40. Found: C, 37.88; H, 5.19; N, 12.77; S, 8.35. IR (KBr): ν(BH) 2551, ν(CO) 1908, ν(C≡N) 1688, ν(CN) 1545, ν(P−O$_{alkyl}$) 963, 983, ν(P=S) 645, ν(P−S) 550 cm^{-1}.

R = R* = (−)-Mentholate. Yield: ca. 50%. Anal. Calcd for C$_{38}$H$_{63}$BN$_7$O$_3$PS$_2$W: C, 47.76; H, 6.64; N, 10.26; S, 6.71. Found: C, 48.03; H, 6.76; N, 10.16; S, 6.62. IR (KBr): ν(BH) 2564, ν(CO) 1912, ν(C≡N) 1694, ν(CN) 1546, ν(P−O) 925, 954, ν(P=S) 662, ν(P−S) 568 cm^{-1}.

R = Ph. Yield: ca. 60%. Anal. Calcd for C$_{30}$H$_{35}$BN$_7$-OPS$_2$W: C, 45.08; H, 4.41; N, 12.27; S, 8.02. Found: C, 44.83; H, 4.53; N, 11.98; S, 7.81. IR (KBr): ν(BH) 2552, ν(CO) 1907, ν(C≡N) 1700, ν(CN) 1546, ν(P−Ph) 1450, ν(P=S) 653, ν(P−S) 518 cm^{-1}.

Crystal Structure of (*R*)-LW(S$_2$PR*$_2$)(MeCN)(CO). Green crystals of (*R*)-LW(S$_2$PR*$_2$)(MeCN)(CO) were grown by slow diffusion of hexane into a saturated dichloromethane solution of the complex. Intensity data for a crystal 0.13 × 0.13 × 32 mm were measured at room temperature (20 °C) on a Rigaku AFC6R diffractometer fitted with graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å. The ω: 2θ scan technique was employed to measure 5741 data up to a maximum Bragg angle of 27.5°. The data set was corrected for Lorentz and polarization effects,[45] and an empirical absorption correction was applied.[46] Relevant crystal data are given in Table 4.

The structure was solved by direct-methods employing SHELXS86[47] and refined by a full-matrix least-squares procedure based on *F*.[45] Non-H atoms were refined with anisotropic displacement parameters and H atoms were included in the model in their calculated positions (C−H = 0.97 Å, B−H = 0.95 Å). The refinement was continued until convergence employing σ weights (i.e., 1/σ^2(F)) for 4040 data with $I \geq 3.0\sigma(I)$. The analysis of variance showed no special features, indicating that an appropriate weighting scheme had been applied. The absolute configuration is based on the conformation of (−)-mentholate. Final refinement details are collected in Table 4, and the numbering scheme employed is shown in Figure 1 (drawn with ORTEP[48] at 40% probability ellipsoids). The teXsan[45] package, installed on an Iris Indigo workstation, was employed for all calculations

Supporting Information Available: Tables of fractional atomic coordinates, thermal parameters, hydrogen atom parameters, all bond distances and angles, and complete ^{13}C NMR data (11 pages). Ordering information is given on any current masthead page.

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